# Progress of Research on Preparation of Micro Gas Sensors of Metal Oxide Semiconductors

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***Abstract***

New progress of research on the preparation technique of micro gas sensors of metal oxide semiconductors is introduced, such as the chemical treatment of the gas sensing film, the deposited technique of gas sensing film in the oxygen radical assisted EB evaporation, the technique of the multilayered film, the fabrication technique of the thermally oxidized, the technique of the electrode configuration, the fabrication technique of the miniaturized arrays by micro-molding in capillaries, the dip-coating of the sol-gel. And their features will be analyzed respectively, and their existing problems and future development directions will be given.

***Keywords***

*Metal Oxide Semiconductors; Gas Sensor; Preparation; Selectivity; Stability*

## Introduction

As a "gas - electric" information conversion device, the metal oxide gas sensor realizing the gas detection and production process control has the quick and simple advantages and a wide application prospect compared with other methods. But with the development of modern agriculture and information technology, People are no longer satisfied with the detection of gas monitoring and alarm, and have raised higher requirements, not only has the qualitative discrimination, but also has a quantitative indication function.

Such as used for air quality detection, food, fragrance, perfume quality evaluation and production process control, the metal oxide gas sensor is also put forward higher requirements, not only high sensitivity, but also requires high gas sensitivity selectivity and stability. In order to solve this problem, since the nineteen sixties, people have developed $SnO_2$, ZnO, $Fe_2O_3$, $In_2O_3$ and other materials, and development of new materials is undoubtedly a very meaningful work. But the gas sensitive properties of gas sensitive materials and how to give full play to come true, is another important topic -- gas sensor preparation technology. In recent years, doping, film forming, heat treatment, structure and so on has caught wide attention[1], This paper will review relevant literatures in recent years about domestic and foreign gas sensor preparation technology from the angle of enhanced sensor gas sensitive selectivity and stability, and put forward the existing problems and the future development direction.

## Preparation of micro gas sensor technology

Metal oxide gas sensor is the type of the surface resistance control, namely, using surface resistance change to detect the various gases. Its working principle is that in the air, the oxygen molecules can be adsorbed on metal oxide semiconductor surfaces, and obtains the electronic and form chemical adsorption of $O_2^-$, $O^-$, $O^{2-}$ from their surfaces. As a result, the surface resistance is increased. When reducing gas is used as a kind of gas detected, contacting gas sensing element surface , these gases and the chemical adsorption oxygen reaction, leading to oxygen atom trapping of electron back to the oxide surface, as a result the surface resistance decreases. When oxidizing gas as detected gas contacts the surface of gas sensor, these gas and chemical oxygen adsorption reaction will take place, and as a result surface adsorption of $O_2$, $O^-$capture more electrons will form more $O^{2-}$, and lead to the surface resistance rising. Preparation of gas sensor technology is preferred gas from the film composition, morphology, structure, electrode material and shape, to improve the thermal response speed to improve the sensitivity, selectivity, stability of gas sensor and improve the gas response and recovery time.

## The surface chemical treatment of gas sensing film

Gas sensitive film surface chemical treatment is one of gas sensitive films doped with, but is distinct from

other original powder doped into films, because existence and distribution of doping in the membrane is not same, so gas sensitive effect is different too.

Wagh[2] et al used the mass fraction of 95% and 5% of $SnO_2$, ZnO powder milling in alcohol for 24h to obtain uniform powder, and added an organic binder solution, modulated into a powder and binder mass ratio of 75 : 25 having a thixotropic slurry, with the electrodes printed on alumina oxide substrate, after drying it, sintered it under 700℃ for 3h. It was immersed in 0.01 molar concentration of the $CuCl_2$ solution for copper processing. Different gas sensors with different doping concentrations will be obtained for various lengths of immersing time. Drying at 80℃, then sintered at 700℃ for 2 hours, gas sensitive film surface oxidation of $CuCl_2$ changes into CuO. When the mass fraction of CuO in the gas sensitive film is 3.68%, the element is highly sensitive to $H_2S$. Sensitivity is increased from 240 of $SnO_2$-ZnO thick film to $6\times10^4$, the optimal operating temperature will decrease from initial 250℃ to 150℃, and the response time from 30min down to 15s, and recovery time is 7 ~ 8min. CuO content is key parameter to improve the component gas sensitive properties. Mechanism analysis is as follows: when the mass fraction of CuO is 3.68%, enough CuO particles provided are uniformly dispersed in $SnO_2$-ZnO film surfaces to form PN nodes. As a result, the component has a very high initial resistance. When contacting $H_2S$ gas detected, the gas sensitive reaction takes place at lower temperatures, CuO changes into CuS, the PN node is damaged, and the resistance decreases rapidly. Thus the elements are highly sensitive to $H_2S$, in addition, relative to the liquefied petroleum gas, carbon monoxide, carbon dioxide, methane with high selectivity. There is a similar Ru treatment that can improve the components of gas sensitivity and selectivity.

## Composite film gas sensor

### *Homogeneous composite film gas sensor*

Baik[3] et al, using $NH_4HCO_3$ and $SnCl_4$ to form $SnO_2$ colloidal solution precipitation, ion removing washed after immersed in aqueous solution, heat it in a pressure cooker in 200 degrees for 2h, formed on the transparent sol solution, taking the trace rotating cover ( 1000r / s ) with interdigital electrode alumina substrate, 100℃ dried for 10 min, repeated for 5 times, forming a 5 layer of homogeneous gas sensitive film, final sintering at 600℃. Gas sensitive tests showed that when $SnO_2$ hot water and sol with the mass fraction of 1.8% rotary cover formed a uniform particle diameter less than 10nm, and a film thickness of 150nm components. At 350℃, the gas volume fraction of $8\times10^{-4}$ $H_2$ has a very good gas sensitivity achieved of 1700 , which is higher than that of the traditional $SnO_2$ sintered body by 2 orders of magnitude. The sensitivity of gas sensitive film prepared by $SnO_2$ water in sol with the mass fraction of 3.2% and 6.1% is less than 250, the particle size increases, and film thickness is 300 and 1000nm. The analysis is that: sol solution concentration is the main factor influencing grain size that is the main factor influencing sensitivity. Multilayer composite membrane suppresses make the size of $SnO_2$ particles, increase and membrane stability and consistency enhance.

### *Heterogeneous composite film gas sensors*

Chan[4] et al used surface micromachining technology to prepare silicon-based film, silicon cantilever for the decline of the heater hot plate (MHP) structure of the gas cell array, the MHP temperature is $300^0$C, the energy consumption is 55mV, and other regional temperatures are still at the room temperature, so it is possible to make the sensor operating circuits integrated on the same substrate. Its uniqueness is that 1nmPt film is deposited before the $SnO_2$ gas sensitive deposited. The composite membrane made of 1nmPt+300nm $SnO_2$ can increase CO gas sensitivity and stability. Lower limit of the gas volume fraction is 1 x 10-6, and CO sensitivity with gas volume fraction of $5\times10^{-5}$ is 16, so there is no floating for the 500 cycle sensitivity test. 1nmPt membrane can effectively restrain the gas sensor in the subsequent heat treatment, and eliminate the influence of the forming process on gas sensitivity and stability of gas sensitive film.

Kwon[5] et al got $In_2O_3$, $Sb_2O_5$ and Pd ultra-fine powder mixtures which $SnO_2$ is main part doped with mass fraction of 10%, 0.5% and 1% by using co-precipitation method. With addition of organic binder, the slurry can be made, and printed in two unit array substrate of Pt electrode alumina. It is dried at 100℃ for 30 min, and sintered at 700℃ for 1 hour. The droplet covers a silicon acid solution to form $SiO_2$ insulating layer of 10 u m. As the gas diffusion control layer, using the same approach in 2 units is respectively covered with a catalytic Pt and Pd layer, dried at 100℃ for 30min, and sintered at 700℃ for 1 hour. Gas sensitivity testing shows that at over 400℃ temperature, the array is highly sensitive to $C_3H_8$ with gas volume fraction of 5 x 10-4, and has a good selectivity to the interference gas CO and $C_2H_5$ via a simple signal processing technology.

Dougami[6] et al used electrophoretic deposition method to make $SnO_2$ sensitive ball with diameter of 150μm or any shape of semiconductor gas surface be deposited uniformly by a oxide coating such as $Al_2O_3$, $TiO_2$, ZnO, $In_2O_3$, $SnO_2$ and $CeO_2$. As a result, the performance of gas sensors has been greatly improved, coating thickness and morphology with the deposition voltage and time can be precisely controlled. This method is convenient for mass preparation, and has good performance

Application of composite membrane technology to improve the sensor's stability and selectivity is catching more and more people's attention. This paper has proposed 4 kinds of typical composite structure preparation technologies such as multilayer homogeneous gas sensitive film, heterogeneous gas sensitive membrane plus catalytic membranes, selective filter membrane and heterogeneity of gas sensitive film. Different gas sensitive material systems, catalytic systems and structure systems based on this will have very large development space. For example, there is literatures[7] reported that $In_2O_3$ gas sensitive film on which 3am Aμ is deposited made the element sensitivity to $10^{-5}NO_2$ increase from 11.9 to 42.6 at 400 ℃.

*Thermal oxidation film forming method*

In low vacuum of 0.1 ~ 2 Torr in argon atmosphere (1 Torr = 133.3224Pa), as-sensing electrode in the stands and the heater on an alumina substrate, Lee[8] et al made low-vacuum thermal evaporation deposition of porous nano-size tin black film with the average particle size of 10nm. Stable nitrogen atmosphere sintering of tin film was performed at 250℃ for 30min, sintering in oxygen atmosphere was performed at 700℃ for 3h to obtain the nano-$SnO_2$ film with high porosity. The gas volume fraction of $1.5\times10^{-3}$ iso-$C_4H_{10}$ has a higher sensitivity at 450℃than that of $CH_4$, $C_3H_8$ and CO gas, and the sensitivity is 17. Black tin deposition of nano-size porous membrane vacuum has greater impact on the gas sensitivity, and sensitivity in low vacuum is as much as 5 times that of high vacuum, the analysis has showed: this low-vacuum preparation of the Sn film of high porosity and small nano-particle size are consistent. Oxide sintering temperature is also an important parameter. Oxidization cannot be completed at temperatures below 700 ℃. Porosity ratio decreases when the temperature is 800℃, and nano-particle size increases, while sensitivity decreases rapidly. The reason is that the recovery time of high porosity gas is longer than that of traditional element (1 ~ 2min), moreover, the recovery time is effectively shortened through reducing the Sn film thickness and raising the test temperature. To get the suitable resistance and improve stability, the membrane is covered by a layer of gas rotating Pt sol, which was sintered and used as a catalyst layer, and the sensitivity varies within 1% during the gas sensing tested for30 days long.

This technology has obvious characteristic: it can enable two processes of oxidating and sintering at the same time, and effectively maintain nano-particle size and high porosity ratio of the gas sensing film. Elements have very high gas sensing stability after catalytically treated.

*Technology of microscopic casting micro sensor array*

Microscopic casting technology, also known as MIMIC, was first used by Heule etc [9], and is one of flexible plane printing technologies. Man-made PDMS with micro-grooves is used as an elastic mold, and the capillary is formed combined with array micro-disk. A linear array of micro-sensors is formed by using the capillary action to carry out micro-casting of liquids or suspension materials. Micro- substrate has the same preparation process as cantilever MHP, and energy consumption is 50mV at 300℃. The shape of gas-sensing electrode depends on the casting mold. MHP includes two sides, and each side is integrated with six pairs of 10μm wide gas electrodes with spacing of 10μm. Micro-shaped grooves are formed in the PDMS by using photolithography corrosion, which are 10μm wide, 30μm long and 6 ~ 7μm high. In addition to ion-water treatment for 2 min, the micro-die chip is put on the micro-plate with electrode under the microscope. The electrode is overlapped with the micro-grooves securely. 10μml $SnO_2$ Nano-suspension with mass fraction of 15% is taken and put at the entrance of the capillary pores, which are filled through capillary action force. They are dried naturally at room temperature for 30min. Then PDMS mold can be gently separated with a clamp. 12 micro-gas sensors are integrated on each MHP. Before the gas-sensing tested, the gas-sensing material is heat treated at 290 ~ 300 ℃ for 24 ~ 48 h, and the peak temperature can occasionally reach 400℃. The sensitivity of CO with gas volume fraction of $2\times10^{-3}$ is more than 10 at 160 ~ 290 ℃, and the lowest gas volume fraction of CO detected is $6\times10^{-4}$. Technology of microscopic casting sensor array has much space of optimization, for example, different gas sensitive material systems and different doping systems will improve gas sensing performance of element,

furthermore, the technology will become a powerful supplement for micro-mechanical manufacturing technology.

### *Sol-gel film forming method*

Tong Mao-song [10] et al used $WCl_6$ (99.95%) as the precursor, isopropyl alcohol as the solvent to prepare the solution with concentration of 5g/100ml. After standing 2d, it changed into a sol, and a ceramic tube of comb-shaped golden electrode deposited was cleaned with acetone, isopropyl alcohol and ionized water in such order, then it was dried at 100 ℃. At room temperature, the ceramic tube was slowly immersed in the sol, and then raised slowly. After the sol hydrolyzes and concentrated, it was dried in the air at 120 ℃ for 15min and heat treated at 500℃ for 10 hours. It has very high sensitivity, good selectivity and quick gas response for trimethylamine (TMA) at 70℃. The low limit of the gas volume fraction is $5\times10^{-5}$. When the gas volume fraction of TMA is larger than $10^{-4}$, the sensitivity of elements will increase linearly with TMA concentration. The sensitivity can reach 36 for TMA with gas volume fraction of 10-3, furthermore, the selectivity is very good because the sensitivity is less than 5 for ammonia, alcohol, gasoline, methane, carbon monoxide and water vapor with the same gas volume fraction. TMA response time for gas volume fraction of $10^{-4}$, $5\times10^{-4}$ and$10^{-3}$ is 2, 2.5 and 6.5s, and recovery time is 21, 24 and 30s respectively. Sol-gel film forming method is a very simple and economical film-forming method. Catalytic doping material can be evenly dispersed in the gas-sensing film, and the film thickness can be controlled by changing the pulling speed. Moreover the film thickness is uniform, the preparation process can be controlled very well, the consistency of element is good, gas-sensing performance is stable. However, heat treatment temperature and time have a greater impact on the gas-sensing properties, should enable the sol-gel film fully crystallized.

### *Problems and Prospects*

In order to improve the selectivity and stability, a lot of research has been carried out and some progress has been made in recent years. But these researches was only for unilateral technology such as new technology of film forming, gas sensitive film processing, structure of composite gas sensitive film, new doping technology and so on. There is a lot of research work to be done: (1) improve selectivity and stability of elements further, (2) improve mechanical stability of elements through effects of temperature and time of heat treatment for gas sensitive materials on the substrate, a heater, adhesive performance of electrode membrane, (3) integrate of micro gas sensor array and packaging technology.

## Conclusion

The development of information technology accelerates demand for gas sensors, and provides mighty power for continuous development of preparation technology of gas sensors. The continuous development of new nano, nano composite materials and microelectronics, micro mechanical manufacturing technology applied in the sensor field will simplify the process, reduce the cost and improve the selectivity and long-term stability of gas sensors. It will cause further miniaturization and large scale integration and "Systematic Biology" compatible to CMOS process for gas sensors.

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